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USE OF CHEMICAL ADDITIVES TO IMPROVE AERATION RATES

Stefan A. Zieminski

Maine University
Orono, Maine

1965

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PROGRESS REPORT NO. I

USE OF CHEMICAL ADDITIVES TO IMPROVE AERATION RATES

by

STEFAN A. ZIEMINSKI

1965

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INTRODUCTION

The mass transfer of oxygen from air bubbles to water is of considerable practical importance in treatment of sewage by bio-oxidation and in many industrial fermentation processes. The cost of this operation is comparatively high because large quantities of air have to be compressed to the pressure of the system and dispersed into small bubbles. The facts that the air contains only about 1/5 oxygen by volume and that the efficiency of oxygen absorption is small are responsible for the large quantities of air used in this process.

Any factor improving the rate of oxygen transfer is therefore of importance in determining the economy of aeration systems.

Some of our previous work (6,25) has shown that considerable increase in the rate of transfer can be achieved by small amounts of some organic substances.

To obtain more information on this action it was proposed to conduct a preliminary investigation of the effects of three homologous series of organic compounds on the size of air bubbles, mass transfer coefficient, and on the interfacial areas of air-water dispersions. The series of compounds selected for investigation were the mono- and di-carboxylic acids and aliphatic alcohols. This was done in order to determine the possible effects of the type of the compound and its molecular size. Some tests on carboxylic acids, obtained in our previous work, are also discussed in this report.

It was proposed to use as the experimental system a swarm of bubbles produced by a porous plate. The disadvantage of this system is the difficulty which it presents to a rigorous mathematical treatment. However, it was realized that the action of these substances is principally due to the ability to prevent coalescence of the bubbles and therefore the study of the swarm of bubbles was a more logical way of investigation. In addition, this system offers the advantage of obtaining data more closely related to the actual aeration practice.

In all the tests presented in this report, the relative effects of the investigated substances are referred to distilled water as the reference base.

REVIEW OF THE PREVIOUS WORK

It has been found that some organic substances present in the aerated liquid may affect the size of the bubbles, the mass transfer coefficient, and the terminal bubble velocities. Braasch and Braasch (1) suggested in their patent a small addition (0.01%) of lactic acid to the yeast wort to decrease the size of the air bubbles from porous air diffusers and thus increase the surface area of absorption. A similar effect was noticed by Pattle (2) when aerating a 0.1% acetic acid solution by means of a porcelain candle. In this case the diameters of the air bubbles were reduced from 2 mm to 0.1 mm. The possibility of formation of a liquid film between the bubbles, which prevents their coalescence, was offered as an explanation.

Verschoor (3) points out that the formation of small bubbles in dilute solutions results not so much from the lowering of surface tension as from the difference between the concentration of the solute in the interface and that in the bulk of the liquid. Such a concentration difference was experimentally demonstrated by Donnan and Baxter as early as 1911 (3).

Carver (4) in his experiments with a Venturi diffuser found a similar decrease in the size of air bubbles when operating with water containing small amount of a detergent.

In addition to their effects on the size of bubbles, some organic substances affect the mass transfer coefficient (K) from the gas bubble to the liquid. Baird and Davidson (11) noticed that small addition of a commercial detergent (Lissapol) to water reduced the K_L value of a CO_2 bubble to about half the value in tap water. They suggest, as a possible reason for this drop, the stagnation

of the rear surface of the bubble caused by the damping of ripples. Although there is in this case a possibility of an interfacial resistance, Cullen and Davidson (12) have not been able to find such a resistance with 0.01% Lissapol solution. The above observation was confirmed by Timson and Dunn (15) with solutions containing 15 ppm of pentapropylbenzene sulfonate. The presence of this substance decreased the K_L values by 67% when operating under low shear, however no effect was noticed in still water experiments. These authors believe that during the ascent of the bubble a concentration difference of the surfactant is developed at the interface which in turn sets up a surface pressure gradient reducing surface circulation. The increased back pressure of gas in the slower circulating surface film is then responsible for the resistance. Later investigations of interfacial surface gradients and their effects on mass transfer coefficient were conducted by Schechter and Farley (17). Holroyd in his studies of aeration rates as applied to sewage treatment (16) found in agreement with Timson and Dunn that the most significant reduction of transfer coefficient in the presence of surfactants occurred in diffused air (bubble) systems. Still water surfaces as well as "heaving" surfaces did not show any appreciable depression of K_L in the presence of surface active agents.

It is also of interest to note that Lieberman in his studies of diffusion coefficients (7) found that the rate of diffusion of a stationary (trapped bubble) is considerably different from free bubbles and that the coefficient is surprisingly independent of contamination of the interfacial boundary between air and water. Similarly Houghton et al. (8) did not find any marked change of diffusion coefficient when 0.05% of Lissapol was added to water. They found also no appreciable difference in diffusion coefficients in pure water and 2.4% sodium chloride solutions. It was suggested that some apparent drops in the rates of absorption in the presence of surface active agents could be due to elimination

of ripples on the liquid film surfaces. Emmert and Pigford (9) found that addition of a small amount of a surfactant can produce such an effect.

The work of Garner (10) throws some light on the effects of surface active agents on drag, circulation and distortion of liquid drops. He found that there was invariably less circulation after contamination with surfactants and that the drops were more distorted. Hence the calculated drag coefficients were higher than for pure water. However, he noticed that in some cases addition of minute quantities of some surfactants can bring about a decrease in distortion.

Presence of surface active agents can also affect the terminal velocities of bubbles rising in liquids. Baird and Davidson (11) noticed that in the case of bubbles of diameters below 1.2 cm the velocity of rise was lower in a dilute Lissapol solution than in pure water.

The effects of surfactants on the over-all rate of absorption ($K_L A$) are of special interest in aeration practice, because they show the combined effects of these substances, on the mass transfer coefficient (K_L) and the total surface area (A).

Carver, when producing air bubbles by means of a Venturi diffuser (4), found that in the presence of small amounts of a surfactant the over-all rate of absorption was increased. In this case, despite reduction of the transfer coefficient, the rate of absorption was improved because of material increase in the surface area produced by the smaller bubbles. A similar observation was made with a porous plate diffuser (5) where addition of a surface active agent (Aerosol O. T.) increased the over-all rate of absorption because of increase of the interfacial area. Zieminski and Hill, studying the effects of some organic substances on the rate of oxygen transfer (6), found in the case of Aloxite (porous) plate a twofold increase of the rate of transfer by addition of only 5 ppm of 4-methyl-2 pentanol to water. In a continuous aeration system this effect can be considerably increased by a continuous addition of the substance directly in the zone of bubble formation.

PROCEDURE

(1) DESCRIPTION OF EQUIPMENT

A schematic diagram of the equipment is shown in Figure 1. The absorption column used in this work was 50 cm high and had a rectangular cross section of 5 cm by 10 cm. The two larger sides of the column were made of lucite and the two smaller walls of a brass channel. The air disperser located at the bottom of the column was made of an Aloxite plate (Grade 2) and was 8 mm in diameter. The top of the disperser was located 5-1/2 cm above the bottom of the column. Compressed air was introduced through a rotameter and a small connecting vessel into the tube leading to the porous plate. A stirrer consisting of a small inclined lucite plate was located below the level of the disperser. The purpose of this stirrer was to achieve a more uniform distribution of the air bubbles in water and thus decrease the error in the determination of the gaseous hold-up. A constant operation of the stirrer was maintained in all the absorption tests.

(2) DETERMINATION OF AERATION RATES

The column was first filled with distilled water to the 2750 ml mark and its temperature adjusted to 25°C. The water was deoxygenated by means of nitrogen. The usual stripping time was about 20 minutes. At the end of the deoxygenation period, the required amount of the investigated substance was added and the flow of nitrogen was continued for a few minutes to insure its uniform distribution. After deoxygenation the first dissolved oxygen sample was taken and the volume of water in the column was adjusted to 2500 ml. The same air flow rate of 68 ml/min (STP) was used in all the tests. At 2 to 3 minute intervals samples of water were taken in 30 ml bottles provided with glass stoppers. The dissolved oxygen in the samples was determined by the micro Winkler method. Four to five samples

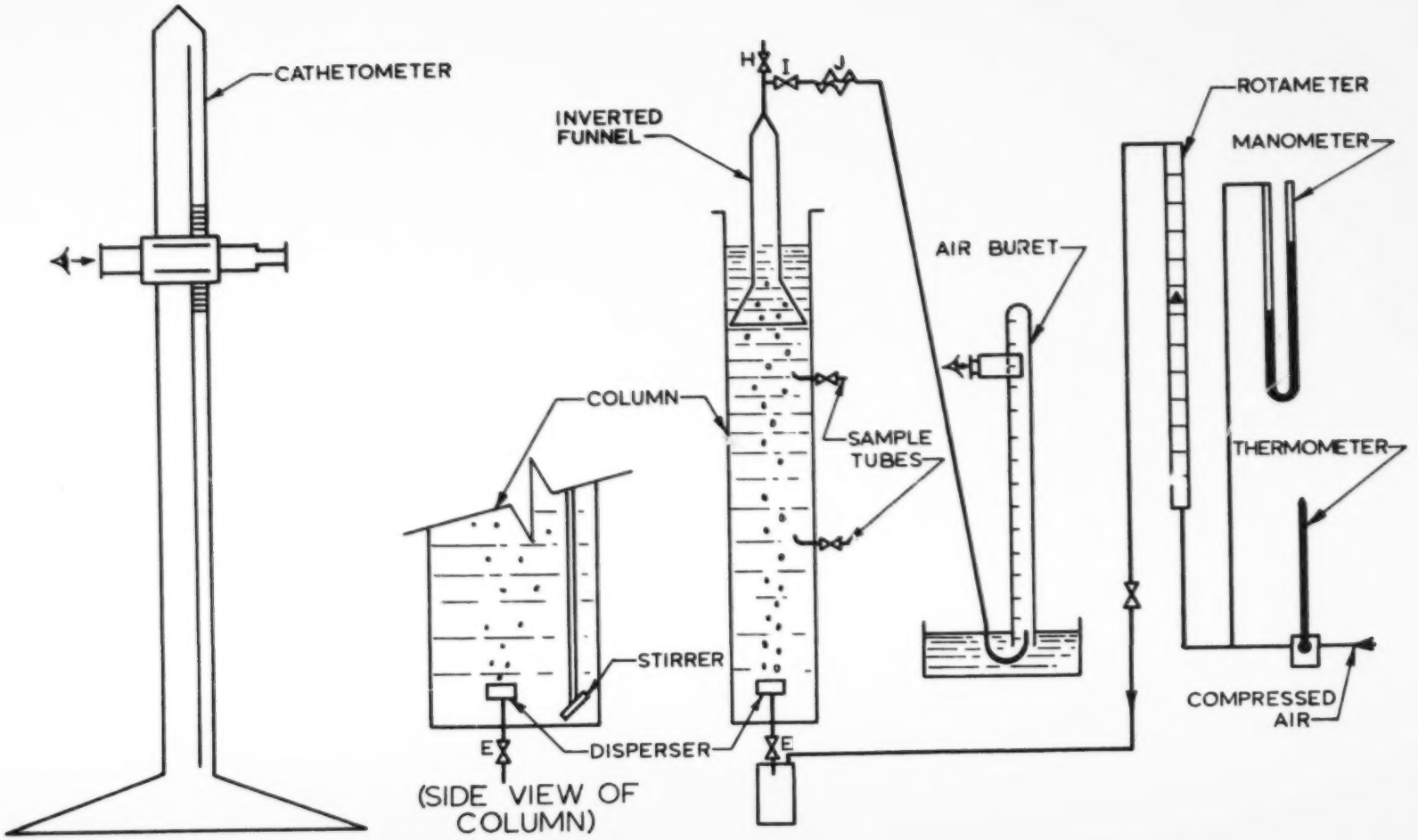


FIGURE 1
TEST EQUIPMENT

were taken during the course of the aeration tests. The results obtained were plotted against time and the resulting absorption curve was used in the calculation of the rate of oxygen transfer.

(3) DETERMINATION OF THE GASEOUS HOLD-UP

The arrangement used in the determination of the gaseous hold-up is shown in Figure 1. It consisted of an inverted funnel with an enlarged stem. The stem of the funnel was provided with glass tubing leading to a gas buret. The measurement of the hold-up was conducted in the following way: The buret was filled with water and valve H was opened. The rate flow of air was adjusted to the required value and the funnel was immersed in the water to a depth of slightly above the top of the cone. In the next step valves E and H were closed instantaneously and valve I opened. The air collected in the funnel was thus introduced through the damping constriction J into the buret. The rise of the level of water in the funnel was observed by means of a travelling microscope. As soon as the water level in the stem of the funnel reached the water level in the column, valve I was closed and the volume of the air collected in the buret was measured. Five readings at four different positions of the funnel were taken, averaged, and corrected for pressure existing in the gas buret. This average was then multiplied by the ratio of the column to funnel areas. This method of gaseous hold-up determination proved to be very reproducible once the technique of operation was mastered. It has the obvious advantage of a direct determination.

(4) DETERMINATION OF THE SIZE OF THE BUBBLES

The bubble size was determined by means of a photographic technique. A Polaroid Model-150 camera with a close-up lens was used in taking the pictures. An electronic flash adapter was attached to the camera and the 1531-A Electronic stroboscope was attached to this adapter. The stroboscope was adjusted so that a

flash of 3 micro-seconds would be produced when the shutter was triggered. Polaroid films Type 46-L or 146-L were used and the resulting transparencies were then projected on a screen. Before the pictures were taken, a rod of exactly 3.14 mm in diameter was inserted in the column at an angle to the axis of the camera so that a part of the rod would be in focus on the picture. The projection of the picture gave a magnification of approximately 18 times. From the total number of bubbles which were in focus, twenty were selected for the measurement. Since the bubbles had the shape of oblate spheroids their major and minor axes were measured. The actual dimensions of the bubbles were determined from the ratio of the projections of the bubble and the rod and the known diameter of the rod.

The accuracy of this technique was checked by means of glass spheres of known diameters and was found to be $\pm 2.3\%$.

(5) THE INTERFACIAL AREA

The interfacial area was calculated for oblate spheroids from the measured major and minor axes of the bubbles and the gas hold-up. The total number of bubbles was calculated by dividing the total hold-up by the volume of a bubble. Subsequent multiplication of the total number of bubbles by the surface area of the spheroid gave the total interfacial area, A:

$$A = \frac{3H\left(2 + \frac{1-\alpha^2}{\alpha} \log_e \frac{1+\alpha}{1-\alpha}\right)}{4b} \qquad (1)$$

where: H = Total air hold-up, cm^3

b = Minor semiaxis of the spheroid, cm

a = Major " " " " "

α = Eccentricity = $\left[1-\left(\frac{b}{a}\right)^2\right]^{1/2}$

A = Total surface area, cm^2

The above equation was programmed into the 1620 IBM digital computer. To evaluate the reproducibility of this procedure, nine tests were conducted in distilled water under the same operating conditions. From these tests the interfacial surface area was found to be 96.1 sq. cm. The probable error attached to this value was ±1.07 sq. cm and the probable error of each determination was ±3.21 sq. cm.

These reproducibility values may be considered as conservative since in the presence of the investigated substances the hold-up was larger and the bubbles more uniform than in pure water. Consequently the probable error of the actual tests would be smaller.

(6) CALCULATION OF THE MEAN TRANSFER COEFFICIENT K_L

The rate of oxygen absorption was calculated from the equation:

$$\frac{dC}{dt} = \frac{10^6}{W} K_L A(C_i - C_L) \qquad (2)$$

where: C is the D.O. concentration, ppm;

t is the time of aeration, hr;

W is weight of water in column, gms;

K_L is the oxygen transfer coefficient based on the liquid film resistance, gms of oxygen per hour per sq cm per unit concentration gradient in ppm;

A is the instantaneous contact area of bubbles, sq cm;

C_i is the equilibrium concentration of oxygen, ppm;

C_L is the concentration of oxygen in water at any time, ppm;

on the assumption that C_i and A are independent of time, integration of the above equation gives

$$K_L = \frac{W}{10^6 A}\left(\frac{\log_e (C_i - C_o)/(C_i - C_L)}{t}\right) \qquad (3)$$

where C_o is the initial D.O. concentration at time t_o.

The assumption that C_i and A do not change with time is not fully justified. The surface area of bubbles varies because of the change in volume caused by absorption and decrease in hydrostatic head. However, these effects are comparatively small since the amount absorbed constitutes only a small fraction of the total volume of the bubble and the effect of hydrostatic head is practically negligible because of the small height of the column of water used in the tests. In addition, the increase in volume of the bubble due to the decreasing hydrostatic head tends to offset the decrease in volume resulting from gas absorption during the rise of the bubble.

The equilibrium concentration C_i, used in this work, was the average value at the level of the aerator and the top of the column.

The logarithmic term of equation (3) was plotted against time on a semi-log graph paper and the slope of the resulting straight line was used to calculate K_L.

After substitution of equation (1) for the total surface area the final expression for K_L becomes:

$$K_L = \frac{4b.W\left(\log_e \frac{(C_i-C_o)/(C_i-C_L)}{t}\right)}{10^6(3H)(2 + \frac{1-\alpha^2}{\alpha} \log_e \frac{1+\alpha}{1-\alpha})} \qquad (4)$$

The reproducibility of K_L determination was checked using the same nine runs which were used previously for checking the reproducibility of the area determination. From these tests K_L for water was found to be 1.64×10^{-4} gms $O_2/(hr)(cm^2)(ppm)$, the probable error attached to this value was $\pm 0.021 \times 10^{-4}$ and the probable error of each K_L determination was $\pm 0.064 \times 10^{-4}$. In some tests the K_L value for water is given as 1.73×10^{-4}. This small difference in K_L values (0.09×10^{-4}) was probably due to some small changes in the operation of the equipment.

(7) THE BUBBLE DIAMETER

The bubble diameter used in this work is the surface-volume mean diameter (18) known also as the Sauter diameter, d_s. It is the diameter of the bubble for which the volume-to-surface ratio is identical with that of the whole dispersion. It idealizes therefore the dispersion assuming it to consist of equal spherical bubbles of diameter d_s defined as:

$$d_s = \frac{6H}{A} = \frac{\sum n\, d^3}{\sum n\, d^2}$$

where H and A are the total gas hold-up and the total interfacial area respectively and n and d are the number and diameter of the bubbles.

DISCUSSION OF RESULTS

SURFACE AREAS AND SIZE OF BUBBLES

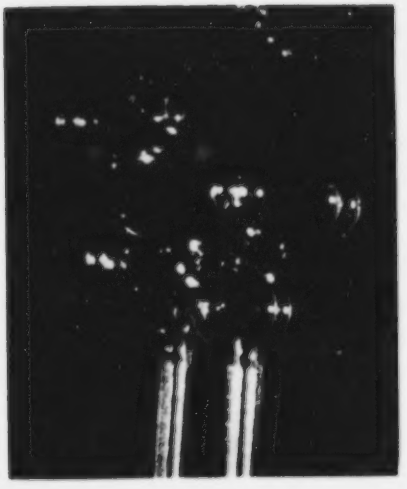
Figures 3 to 9 show the effects of the selected organic acids and alcohols on the total interfacial areas and sizes of the air bubbles. The first two graphs (Figs. 3 and 4) show the effects of mono-carboxylic acids on the surface areas of bubbles. As can be seen they all affect the surface area but this effect increases progressively with the length of the carbon chain. While formic acid at a concentration of 100 ppm shows practically no effect, the octanoic acid at a concentration of only 10 ppm increased the surface area by over 700% of that in pure water. Some inconsistency in the behavior of the decanoic acid could have been caused by its low solubility and by the fact that some of the absorption tests were conducted at concentrations close to the saturation point.

The di-carboxylic acids (Figure 5) showed a behavior similar to that of

(a) Air Bubbles in Pure Water

(b) Air Bubbles in Dilute Butanol Solution

(c) Air Bubbles in Pure Water Speed: 2000 fps



(d) Air Bubbles in Dilute Butanol Solution Speed: 2000 fps

Figure 2.

Air Bubbles in Water and in Dilute Butanol Solutions.

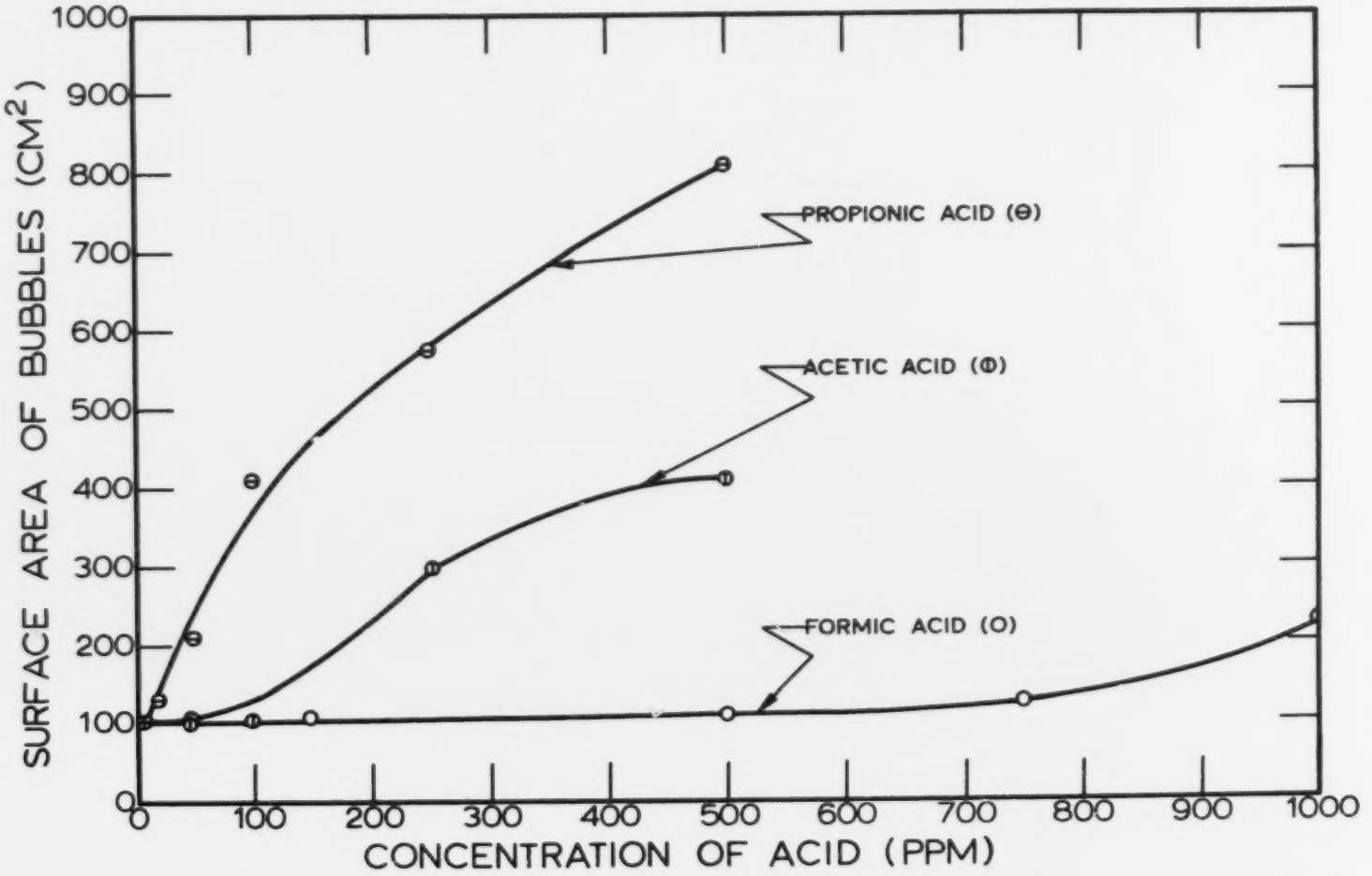


FIGURE 3
SURFACE AREA OF BUBBLES vs CONCENTRATION OF ACID

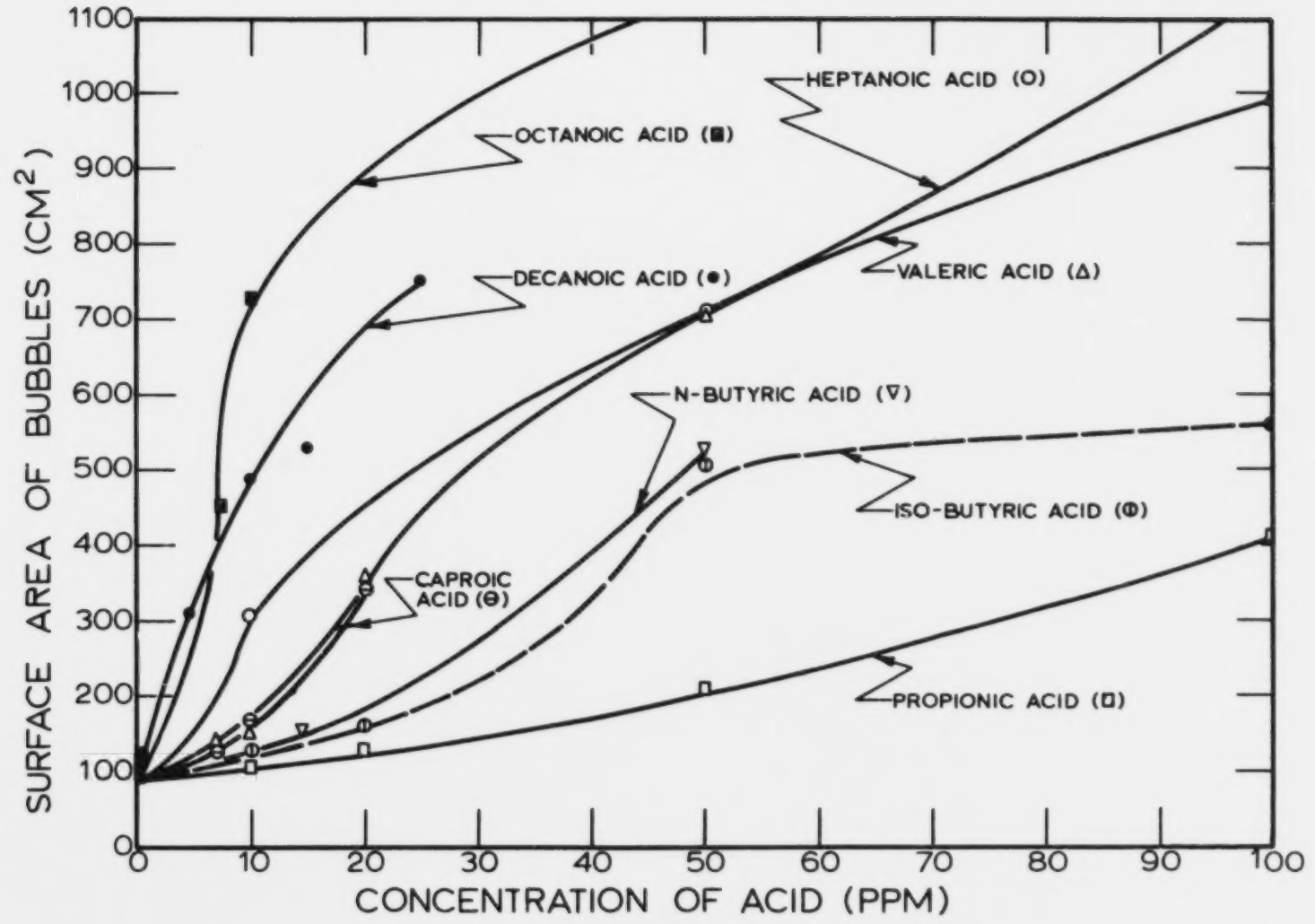


FIGURE 4
SURFACE AREA OF BUBBLES vs CONCENTRATION OF ACID

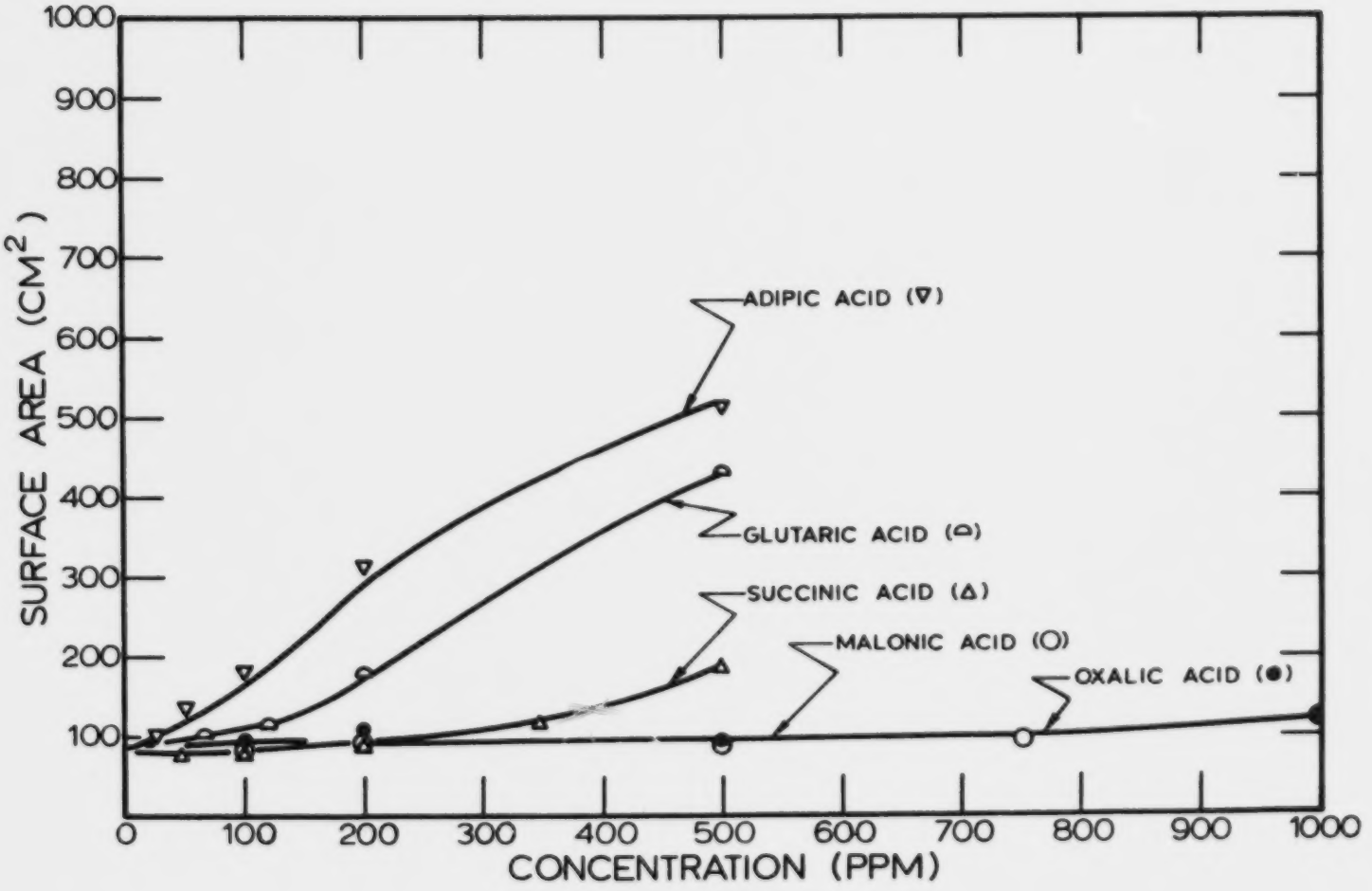


FIGURE 5
SURFACE AREA OF BUBBLES VS CONCENTRATION OF ACID

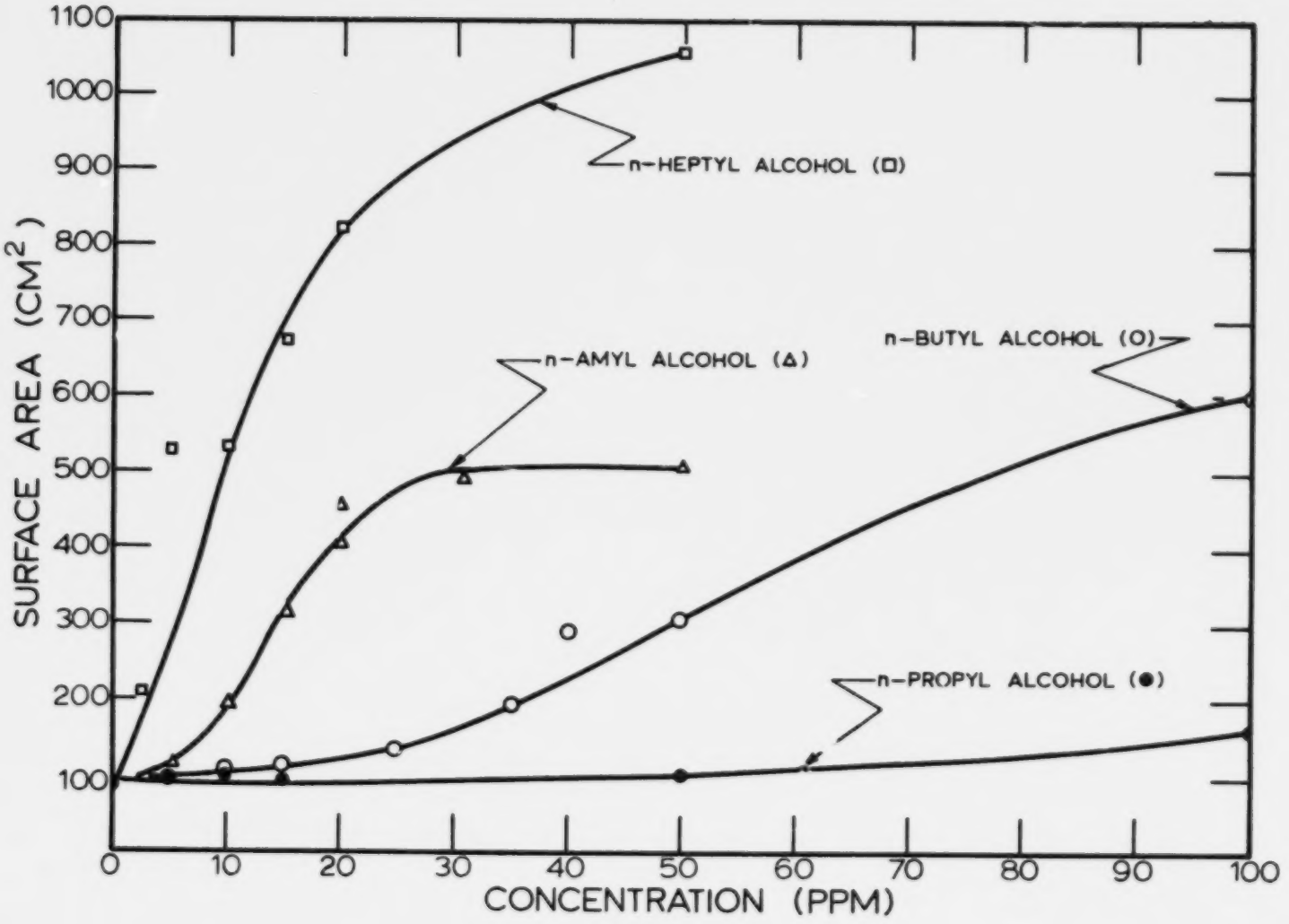


FIGURE 6

SURFACE AREA OF BUBBLES VS CONCENTRATION OF ALCOHOL

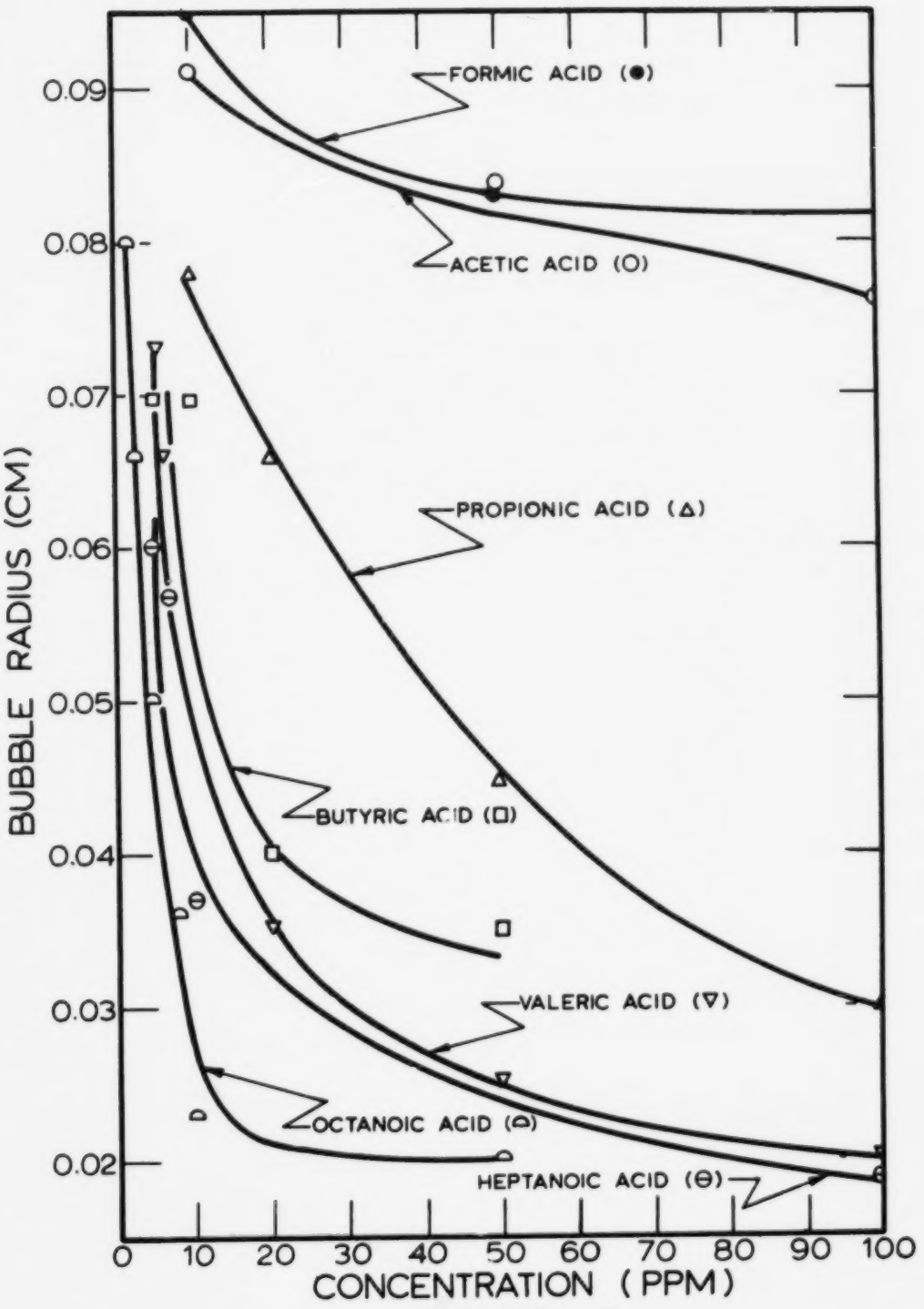


FIGURE 7
BUBBLE RADIUS VS CONCENTRATION OF ACID

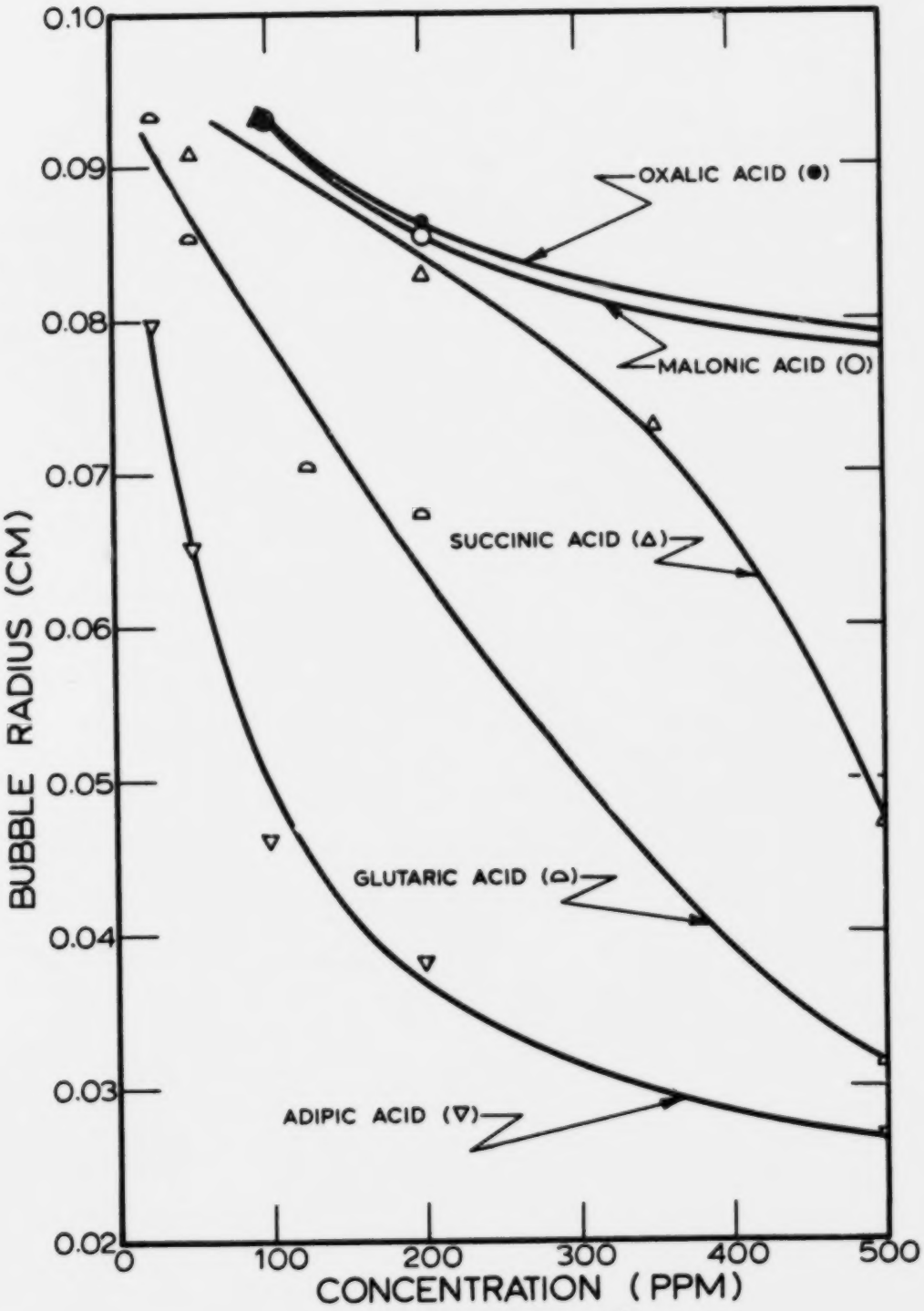


FIGURE 8

BUBBLE RADIUS VS CONCENTRATION OF ACID

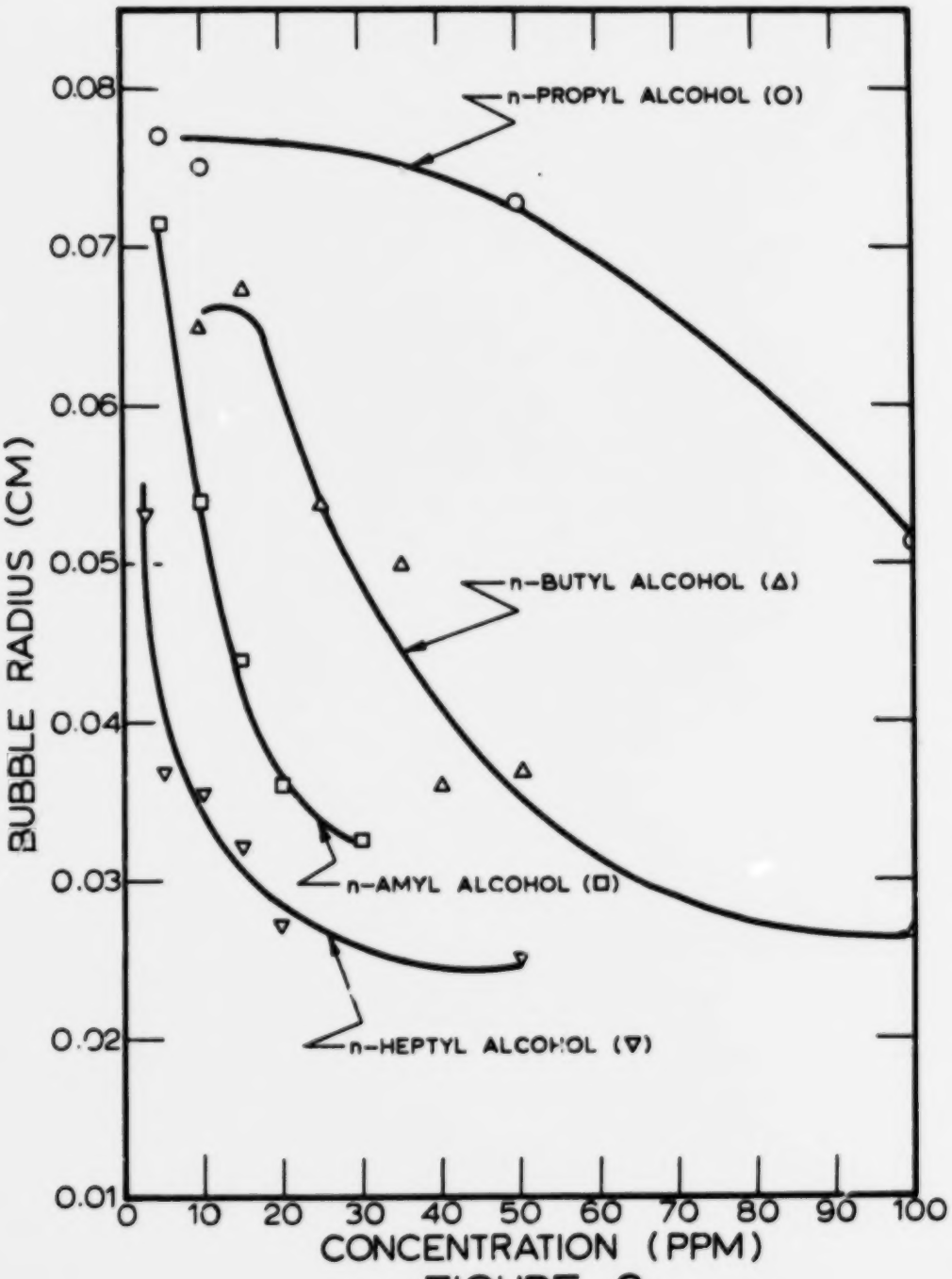


FIGURE 9

BUBBLE RADIUS VS CONCENTRATION OF ALCOHOL

the mono-carboxylic acids; however the magnitude of this effect was much smaller. Over 400 ppm of glutaric acid was necessary to produce the same effect as that of valeric acid at a concentration of 15 ppm only.

The four investigated alcohols (Figure 6) also showed a similar behavior. The effects of the alcohols increased progressively with their molecular weights. Their absolute effects on the surface area of bubbles were however more pronounced than those of di-carboxylic acids approaching in magnitude the effects of mono-carboxylic acids.

Figures 7, 8 and 9 show the changes in the size of the bubbles on addition of small amounts of alcohols, mono-, and di-carboxylic acids. As could be expected the same general behavior can be seen as in the case of interfacial surface areas. Again the effects of each of these groups of compounds increase progressively with the length of the carbon chain and are more pronounced for mono-carboxylic acids and alcohols than for the di-carboyxlic acids. It should also be pointed out that in most cases there is a sharp initial drop in size of the bubbles and that the curves level off when the amount of the substance is increased. Figures 2 a and b show the pictures of the bubbles as taken in pure water and in a solution containing 40 ppm of n-butyl alcohol. It can be seen that the alcohol not only produces a drastic change in the size of bubbles but also decreases considerably their degree of distortion.

It appears that the increase in the surface area of the bubbles results mainly from their decreased coalescence in the presence of the investigated substances. This effect is clearly visible in Figure 2 c and d. The pictures were taken with the Hycam high speed camera at the speed of 2000 f.p.s. The bubbles were produced in water (Figure 2c) and in dilute n-butyl alcohol solution (Figure 2d) by passing air through two glass capillaries located close to one another. It can be seen that in the pure water the bubbles coalesce with formation

of one irregular large bubble. The rate of coalescence of these bubbles was so fast that the speed of 2000 f.p.s. was still too slow to follow the stages of the coalescence. On the other hand, in the presence of a small amount of the alcohol no coalescence occurred and the bubbles were much more uniform in size and free of distortion.

We can imagine the coalescence of the bubbles to occur in two consecutive steps. First the liquid drains from the space between the walls of the two approaching bubbles until a certain minimum (critical) film thickness is reached at which the second step occurs, that is the film ruptures and the bubbles coalesce. The rate of coalescence of the two approaching bubbles will therefore depend among other factors on the rate of drainage of the continuous phase between the bubbles and on the thickness and strength of the remaining film (19).

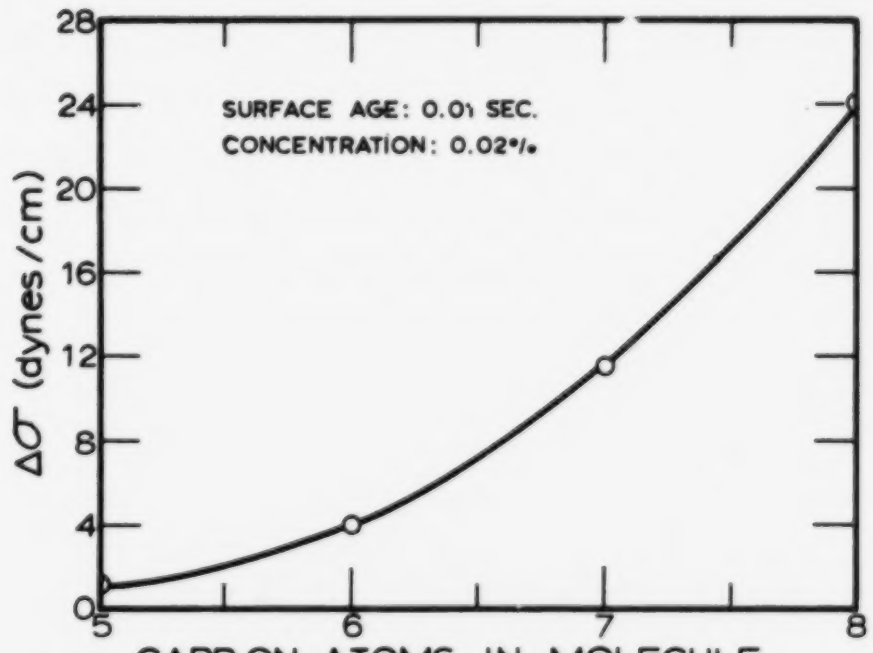
It appears possible that the molecular orientation of the polar-nonpolar solutes at the bubble interface and the resulting attraction of the polar groups to water affect the thickness of the film and its rate of drainage. Foulk and Miller (20) in their "two-bubble" experiments measured the percentage of "film formation" in terms of the number of times in a hundred that the bubbles failed to coalesce. They found that this quantity is a function of the difference between the dynamic and static surface tensions, and the greater this difference the more pronounced is the "film formation" and therefore the smaller the coalescence.

From the above discussion it seems that the large surface areas and the small bubbles produced in the presence of the investigated solutes were due to this difference in surface tensions.

The fact that the effects of these substances (acids and alcohols) on the size of bubbles increased with the length of the carbon chain can probably be explained by the results of the measurements of the dynamic surface tensions

conducted by Addison (21,22,23,24). Using his data on the dynamic surface tensions of 0.02% alcohol solutions at surface age of 0.01 sec and the corresponding equilibrium surface tensions, the surface tension difference, $\Delta\sigma$, was calculated and plotted against the number of carbon atoms in the molecules of the alcohols. The enclosed plot shows the values of $\Delta\sigma$ for the range of n-amyl to n-octyl alcohols.

An inspection of this plot indicates that the differences between the dynamic and static surface tensions increase rapidly with the length of the carbon chain. The above behavior appears therefore to be consistent with the decrease of coalescence and the resulting increase of surface area of bubbles with the length of the carbon chains of the solutes investigated in this work.



$\Delta\sigma$ vs CHAIN LENGTH OF ALCOHOLS

THE MASS TRANSFER COEFFICIENT K_L

The values of the mass transfer coefficients are shown in Figures 10, 11, 12 and 13. Because of the great difference in the effects of the mono-carboxylic acids on K_L, the formic, acetic and propionic acids were plotted separately. Figures 10 and 11 show the effects of the normal mono-carboxylic acids and the subsequent Figures 12 and 13 present the effects of the di-carboxylic acids and normal alcohols respectively.

An inspection of Figures 10 and 11 shows that except for the two highest acids (octanoic and decanoic) the values of K_L first increase with concentration of the acid and then drop well below the corresponding value for distilled water. It is of interest to note that again in this case the magnitude of these effects depends on the length of the carbon chains of the acids. The positions of the maxima in the initial parts of the curves shift progressively to the region of lower concentration with the increase of the molecular weight of the acids. The maximum for formic acid occurs at a concentration of 750 ppm, for the propionic acid at 50 ppm and for the butyric and heptanoic acids at 20 and 7.5 ppm respectively. It is possible that a similar maxima occur also in the case of the octanoic and decanoic acids but at concentrations below those investigated in this work. It is also of interest to note the large magnitude of this effect, e.g., in the case of heptanoic acid at a concentration of only 7.5 ppm the value of K_L increased from 1.64×10^{-4} for pure water to 2.30×10^{-4}, an increase of 40%.

Further increase of the concentrations above those corresponding to the maxima brings a decrease of the K_L values which eventually drop well below that for pure water. This decrease of the K_L in the region of higher concentration appears again to be a function of the length of the carbon chain of the investigated mono-carboxylic acids. For a given concentration the depression of K_L

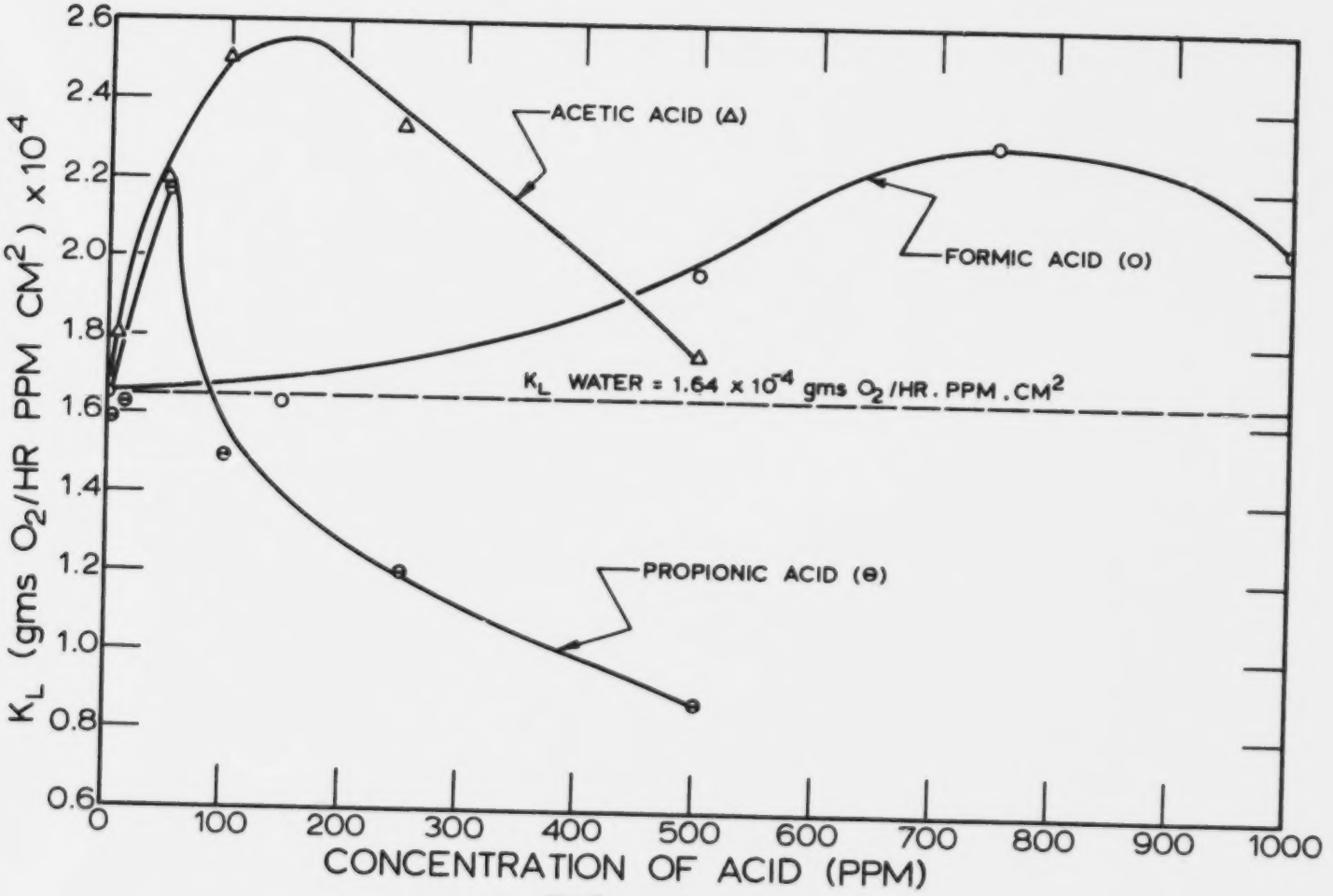


FIGURE 10
K_L vs CONCENTRATION OF ACID

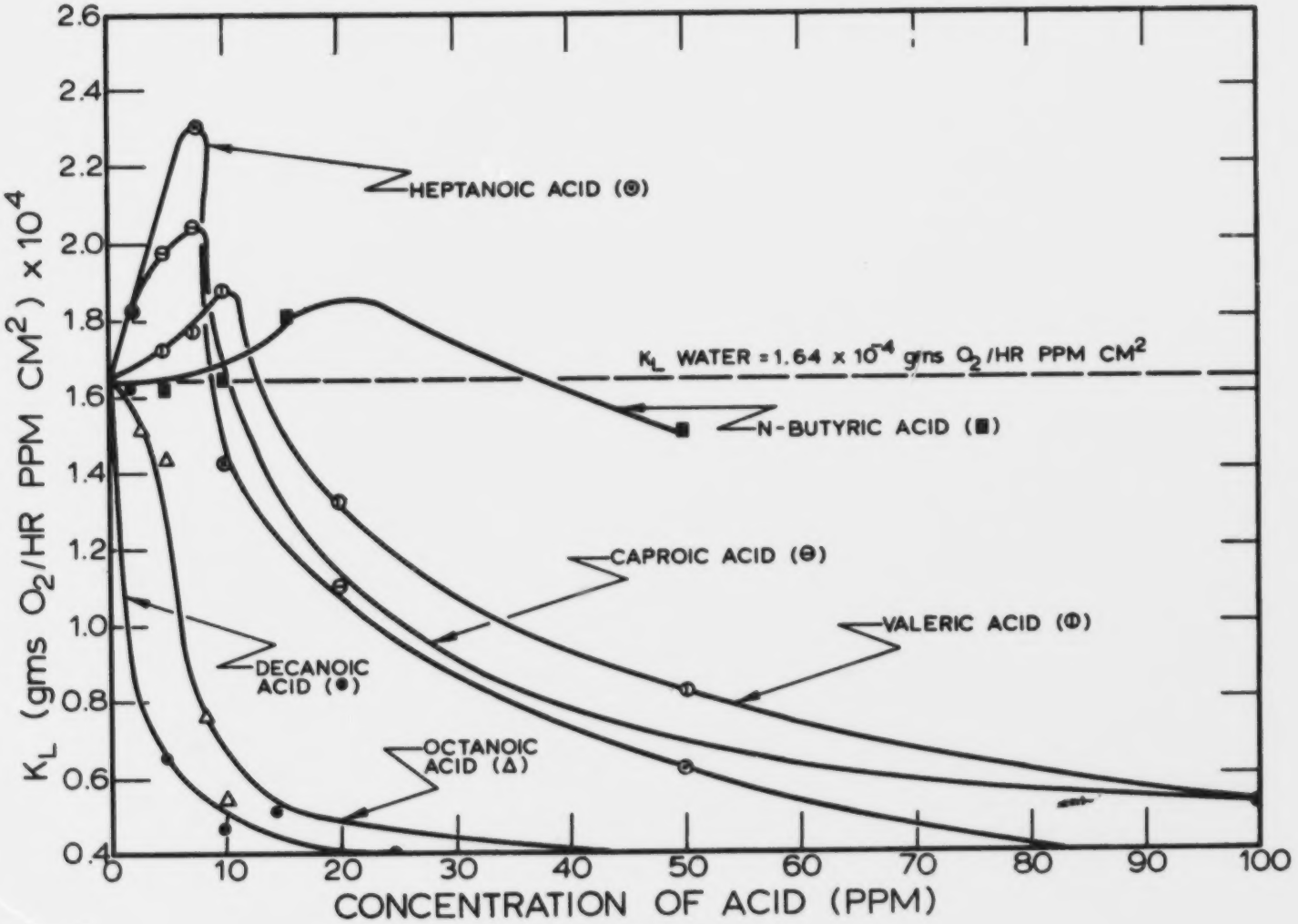


FIGURE 11
K_L vs CONCENTRATION OF ACID

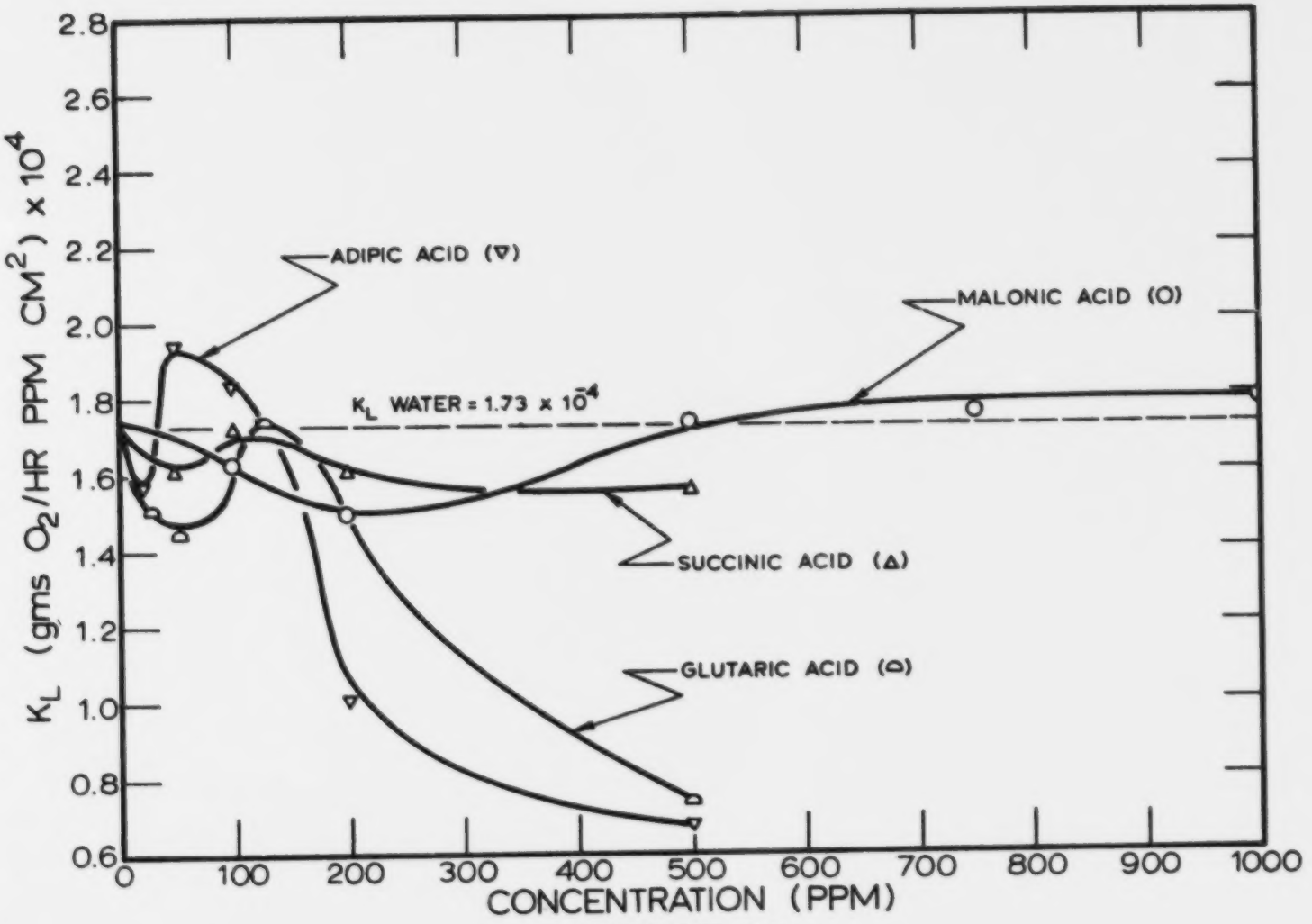


FIGURE 12
K_L vs CONCENTRATION OF ACID

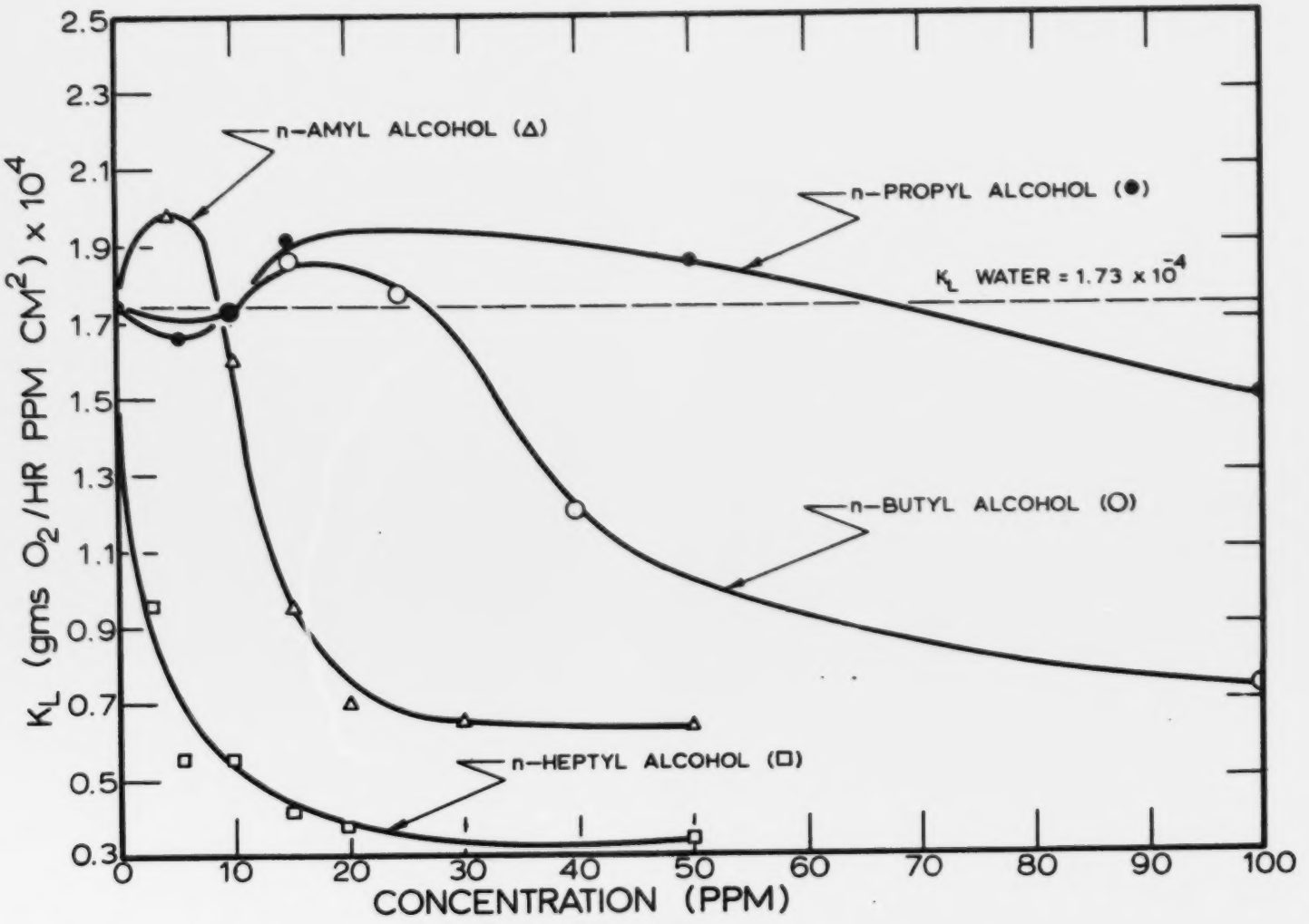


FIGURE 13
K_L vs CONCENTRATION OF ALCOHOL

values increases progressively with the increase of the molecular weight of the acid.

The effects of di-carboxylic acids and normal alcohols are shown in Figures 12 and 13 respectively. The behavior of alcohols is very similar to that of the mono-carboxylic acids. The same shift of the maxima and the progressively increasing depression of K_L values with the increase of the length of the carbon chain can be seen in Figure 13.

The effects of the four di-carboxylic acids are shown in Figure 12. Again a similar dependence of these effects on the molecular weight of these acids can be seen from the figure. However, the magnitude of these effects is much smaller than in the case of mono-carboxylic acids and alcohols. There also appears to be a small initial drop of the K_L values which was absent in the case of mono-carboxylic acids.

Comparing the effects of the various substances investigated in this work on the bubble size and K_L values one cannot but notice the similarity of these effects.

At a given concentration the size of the bubbles decreases progressively with the increase of the length of the carbon chain in any of the investigated groups of compounds. The same applies to the mass transfer coefficient where a similar progressive decrease of the K_L values can be observed in the region of higher concentrations. It seems likely that the formation of a stable film around the bubble, which was already discussed in connection with coalescence, is also responsible for the decrease in K_L.

A more comprehensive investigation would have to be conducted to explain the mechanism of these effects. However, the results of this work indicate that essentially the problem is that of surface chemistry and that the quantities such as the type and size of the molecule and the concentration of the solute are the basic factors.

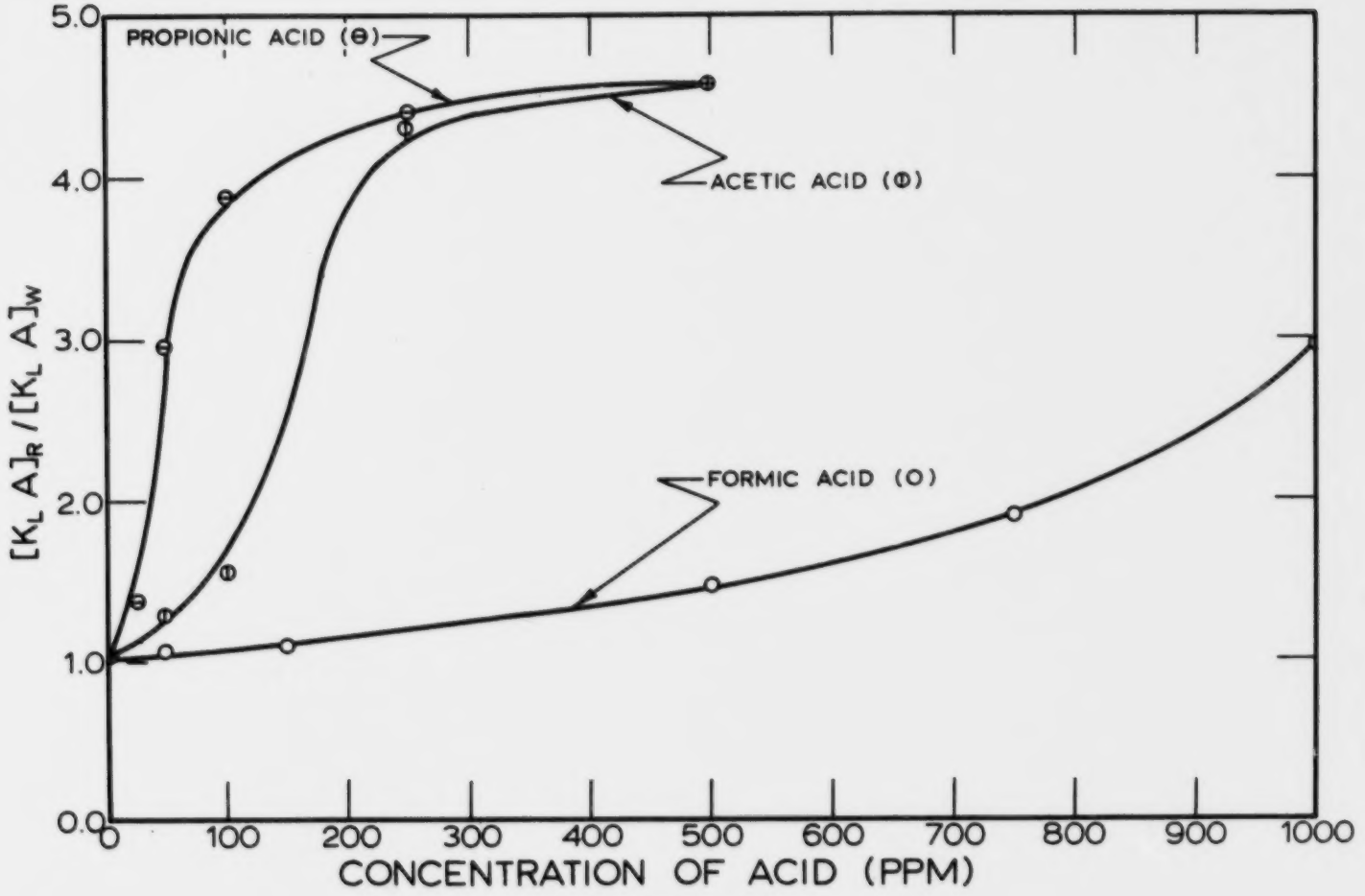


FIGURE 14
$[K_L A]_R / [K_L A]_W$ vs CONCENTRATION OF ACID

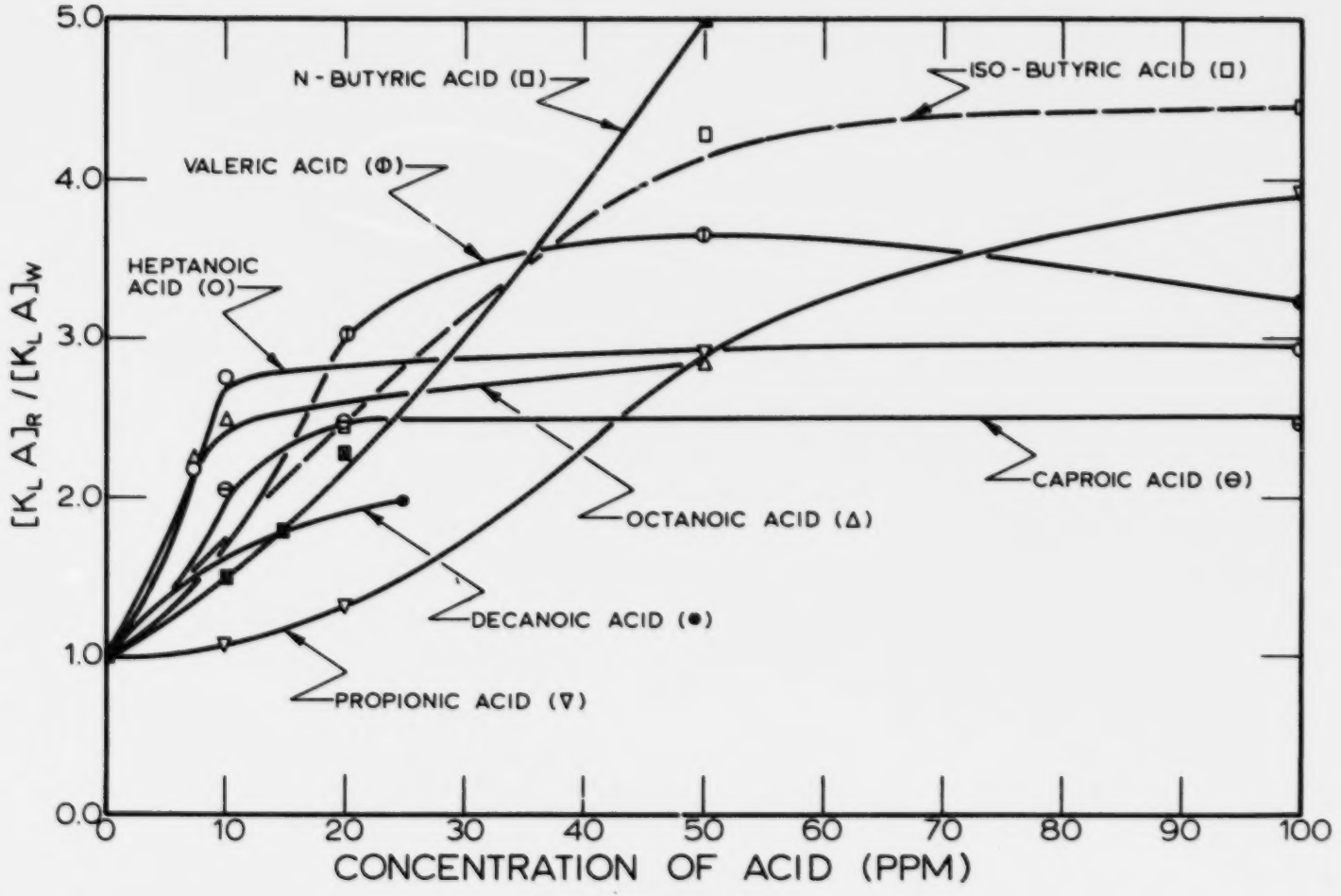


FIGURE 15
$[K_L A]_R / [K_L A]_W$ vs CONCENTRATION OF ACID

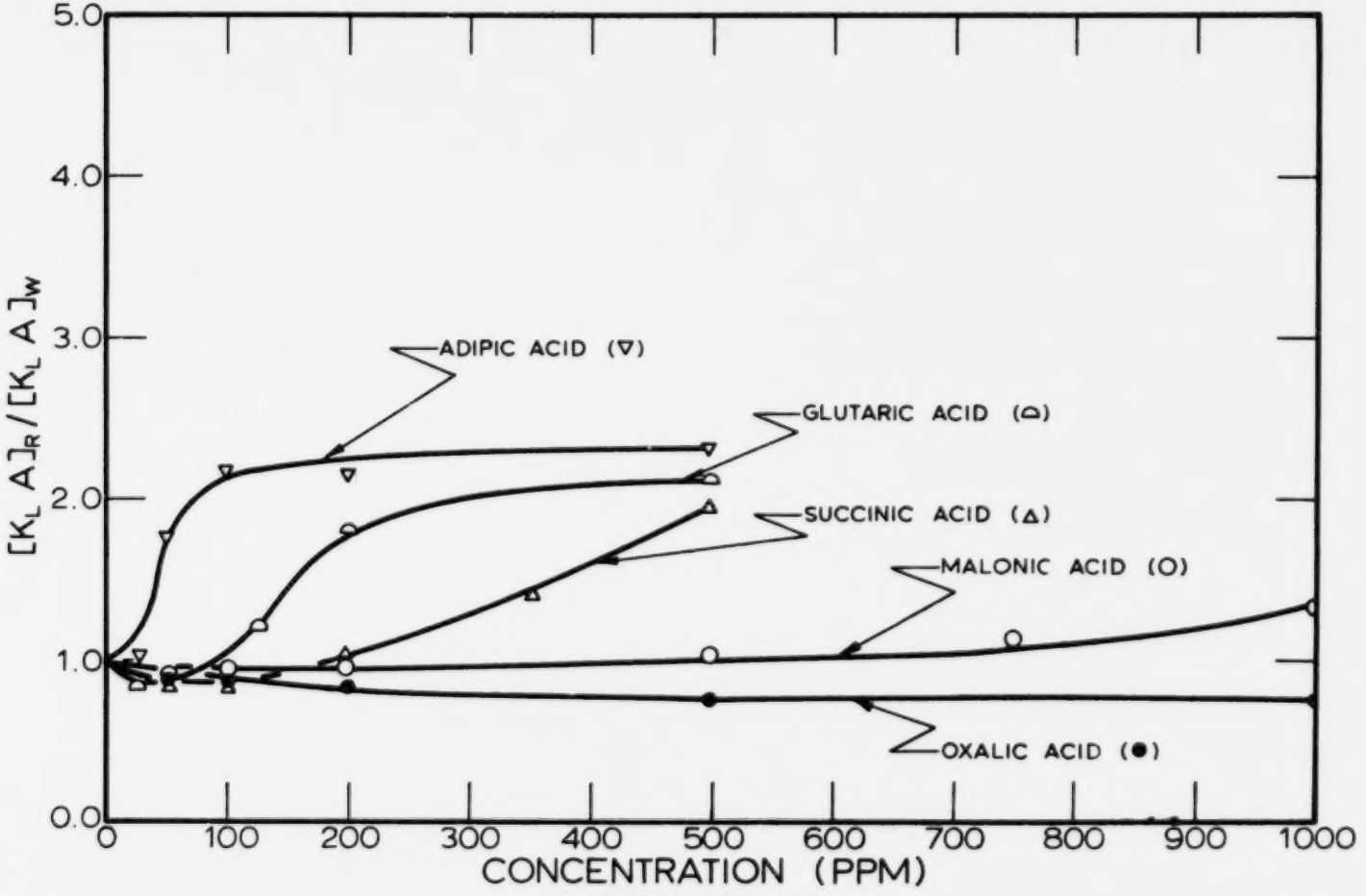


FIGURE 16
$[K_L A]_R / [K_L A]_W$ vs CONCENTRATION OF ACID

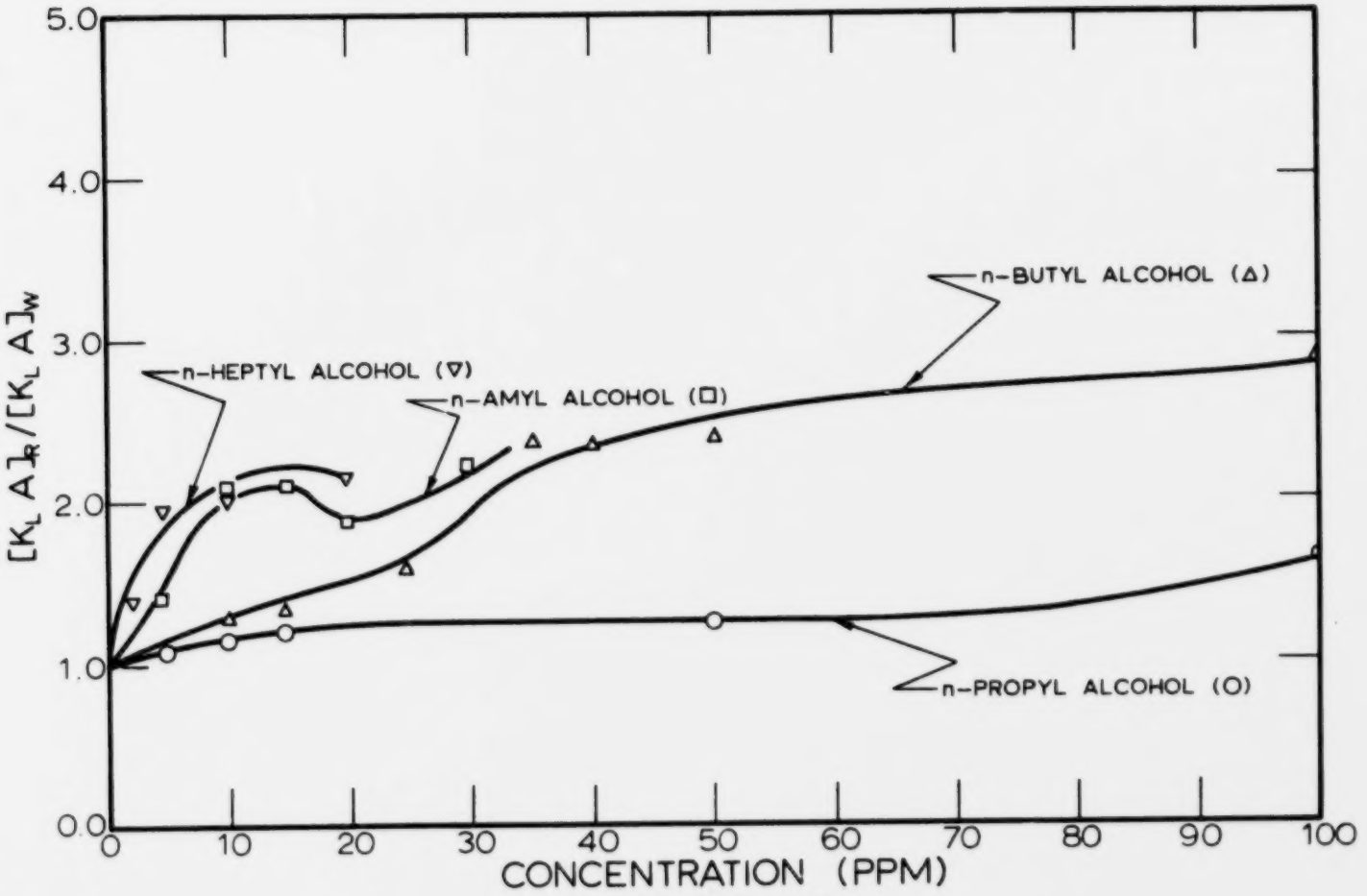


FIGURE 17
$[K_L A]_R/[K_L A]_W$ vs CONCENTRATION OF ALCOHOL

THE TOTAL TRANSFER RATE $K_L A$

The total transfer rate is the rate of oxygen absorption through the total (instantaneous) surface area A. It is a quantity of considerable practical importance since it is a measure of the combined net effect resulting from the changes in the mass transfer coefficient and in the surface area of absorption. Any means resulting in an increase of this quantity will reduce the costs of the aeration plant and decrease the energy requirement of the process. The fact that $K_L A$ does not contain the error involved in the surface area determination is another advantage of this quantity.

The effect of a solute on the total rate is best expressed in terms of the ratio $[K_L A]_R / [K_L A]_W$, where the subscripts R and W refer to the solution and distilled water respectively. Figures 14 through 17 give the changes of the $[K_L A]_R / [K_L A]_W$ values resulting from the presence of the three investigated groups of substances.

The effects of the normal mono-carboxylic acids are shown in Figures 14 and 15. An inspection of these curves shows the pronounced effect of these acids on the rate of transfer. They show also the dependence of this effect on the length of the carbon chain of the acids. On the whole it may be said that the higher the molecular weight of the acid the more pronounced is the improvement of the rate in the low range of concentrations. Thus the propionic acid at a concentration of 10 ppm has practically no effect on the rate of oxygen transfer while the heptanoic acid at the same concentration increases the rate by 180%. This, however, does not apply to the region of higher concentration. While the effect of the heptanoic acid levels off at concentrations higher than 10 ppm, the effect of the propionic acid increases progressively with concentration giving an increase in the rate of transfer of 350% at 500 ppm at which concentration its effect appears to reach a constant value.

Figures 16 and 17 show the effects of the di-carboxylic acids and alcohols respectively. Again, as in the case of mono-carboxylic acids, their effects on the $K_L A$, in the initial concentration range, increase sharply with the length of their carbon chains. While n-heptyl alcohol at a concentration of 20 ppm increases the rate by over 100% the n-propyl alcohol at the same concentration increased the rate of transfer by only 25% over than in pure water. However, this difference in effectiveness becomes gradually smaller at higher concentrations. As can be seen from this discussion, even at a very low concentration (7 to 15 ppm) some of these substances more than double the rate of absorption.

Our previous investigations (6) indicate that the effect produced by a given solute depends mainly on its concentration in the zone of bubble formation and once small bubbles are formed they do not coalesce even when the concentration of the solute in the bulk of the liquid is negligible. Thus injecting a solution of 4-methyl-2-pentanol at the surface of a porous-plate diffuser, it was possible to obtain a 50% increase of the rate at a bulk concentration of 1 ppm only (6).

It must be stressed that the values of $[K_L A]_R / [K_L A]_W$ are not absolute but even for the same solute and concentration depend, to a great extent, on the air dispersing system. It seems that the principal action of the investigated substances is in preventing the coalescence of the bubbles. The greater therefore, in a given system, is the possibility of coalescence the more effective is the substance.

THE EFFECT OF THE MOLECULAR STRUCTURE

To evaluate the effects of the chemical structure on the size of bubbles, K_L, and the interfacial area of dispersion a series of tests was conducted with normal, iso, and tertiary butyl alcohols. The results of these tests are given in Figures 18 to 21.

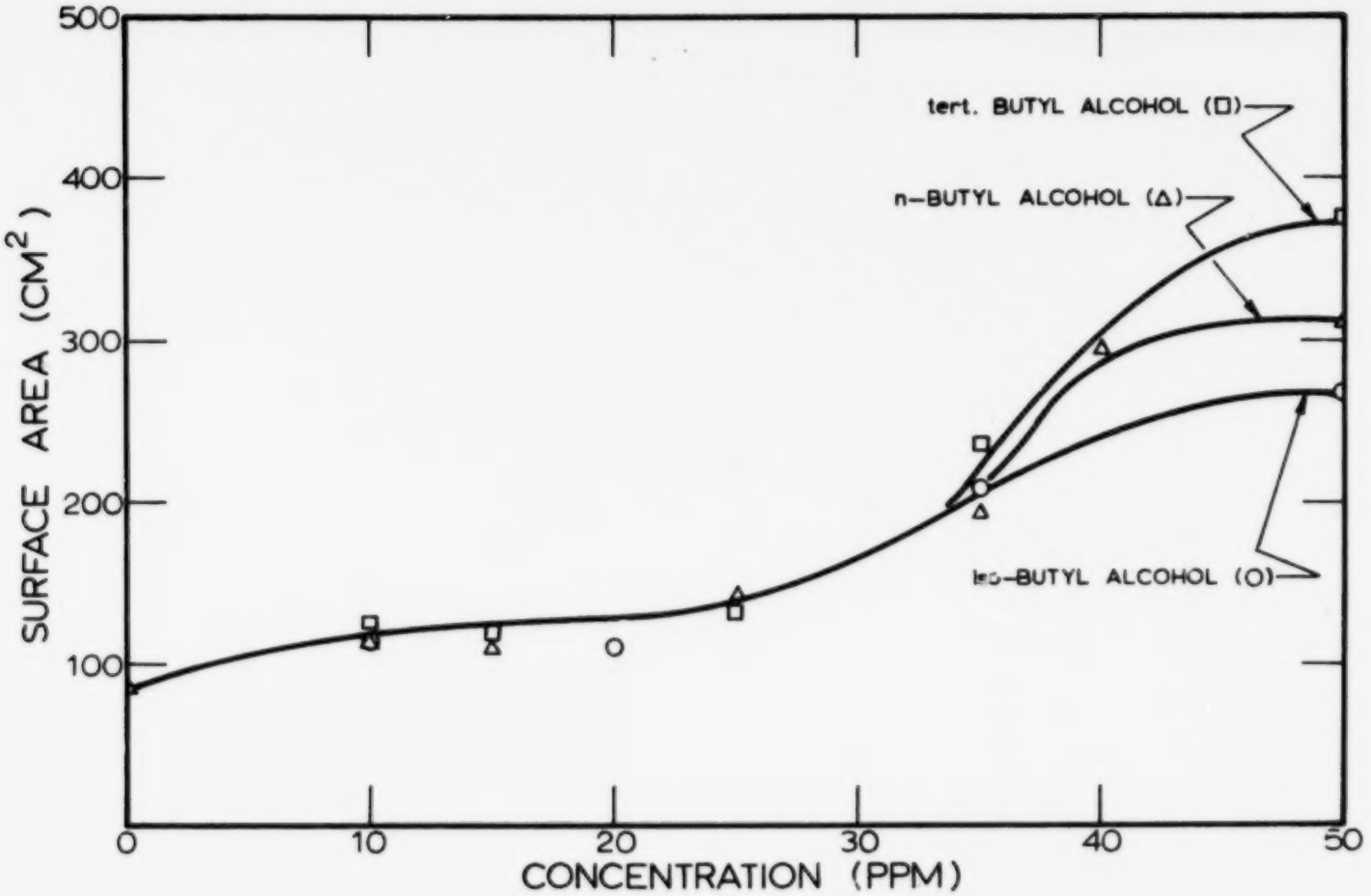


FIGURE 18

SURFACE AREA OF BUBBLES vs CONCENTRATION OF ALCOHOL

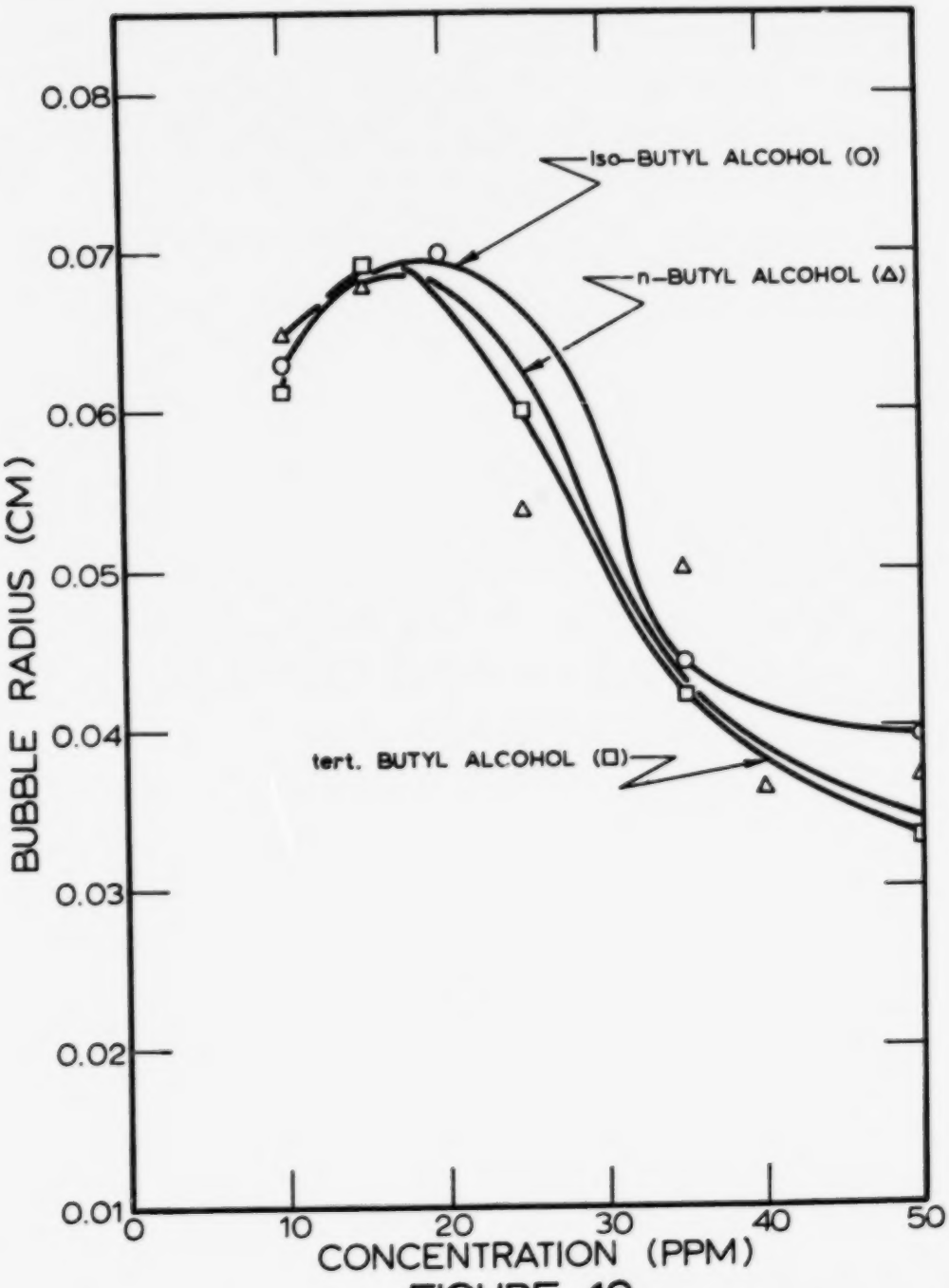


FIGURE 19
BUBBLE RADIUS vs CONCENTRATION OF ALCOHOL

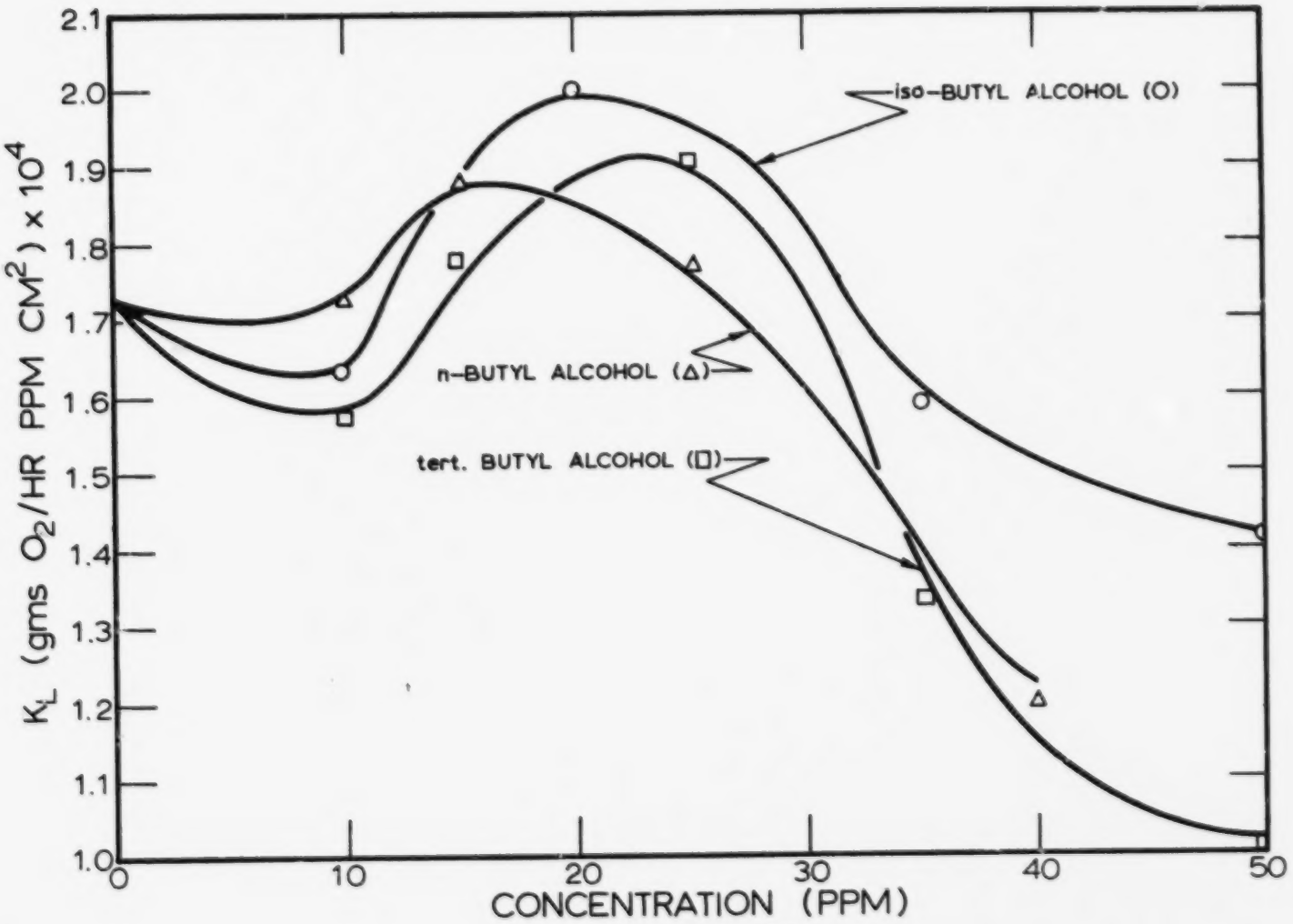


FIGURE 20
K_L vs CONCENTRATION OF ALCOHOL

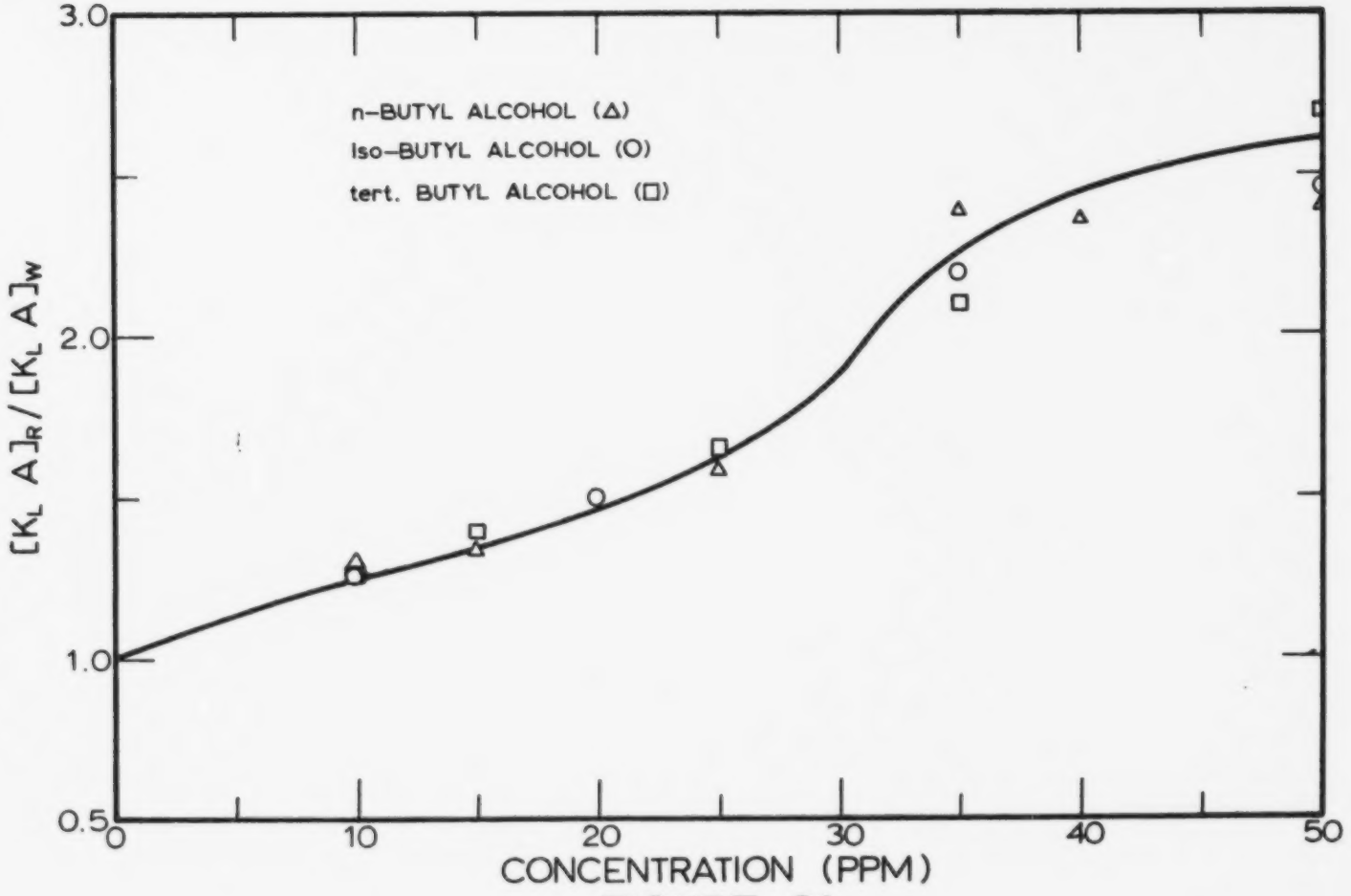


FIGURE 21

$[K_L\ A]_R/[K_L\ A]_W$ vs CONCENTRATION OF ALCOHOL

Inspection of these figures shows that in a lower concentration range (below 35 ppm) there is no appreciable difference in the effects of the isomers on the mass transfer coefficient, size of bubbles or the over-all rate of oxygen transfer. There appears, however, some spread of the results at concentrations in the range between 40 and 50 ppm. The results indicate that the magnitude of the effects of the structure of the isomers is small at least insofar as this group of alcohols is concerned.

SUMMARY

(1) The mono- and di-carboxylic acids as well as aliphatic alcohols decrease considerably the size of the air-bubbles, thus increasing the interfacial surface area of air-water dispersions. The magnitude of this effect is similar in the case of mono-carboxylic acids and alcohols but is much smaller for di-carboxylic acids. In all cases this effect increases progressively with the length of the carbon chain of the compound. The magnitude of this action can be illustrated by the effect of the octanoic acid which at a concentration of 10 ppm increased the surface area by over 700% of that in pure water. The possible explanation of this effect is discussed.

(2) The effects of these substances on mass transfer coefficient also show a consistent pattern. Except for the decanoic and octanoic acids the values of K_L first increase with concentration and then drop well below that for distilled water. The position of the maxima (low concentration range) and the subsequent drops of the K_L values in the region of higher concentrations were found to be functions of the length of the carbon chain in each of the investigated groups of compounds.

(3) The total transfer rate K_LA may be profoundly affected by some of the investigated substances, e.g., the heptanoic acid at a concentration of 10 ppm

increased the rate of oxygen transfer by 180%. In the range of low solute concentration this improvement in the rate is more pronounced the higher is the molecular weight of the substance in each of the investigated groups of compounds. It is emphasized that the effects discussed in this report depend on the air dispersing system. Since the principal action of the substances appears to be in preventing the coalescence of the bubbles, their effectiveness will improve in systems where the possibility of coalescence is greater.

(4) Tests conducted with the normal, iso-, and tertiary butyl alcohols did not show any pronounced difference in their effects on size of the air bubbles and the rate of oxygen transfer.

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